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## Peeling the Astronomical Onion

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## Journal Name

## ARTICLE

## Peeling the Astronomical Onion

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Water ice is the most abundant solid in the Universe. Understanding the formation, structure and multiplicity of physicochemical roles for water ice in the cold, dense interstellar environments in which it is predominantly observed is a crucial quest for astrochemistry as these are regions active in star and planet formation. Intuitively, we would expect the mobility of water molecules deposited or synthesised on dust grain surfaces at temperatures below 50 K to be very limited. This work delves into the thermally-activated mobility of H<sub>2</sub>O molecules on model interstellar grain surfaces. The energy required to initiate this process is studied by reflection-absorption infrared spectroscopy of small quantities of water on amorphous silica and highly oriented pyrolytic graphite surfaces as the surface is annealed. Strongly non-Arrhenius behaviour is observed with an activation energy of 2 kJ mol<sup>-1</sup> on the silica surface below 25 K and 0 kJ mol<sup>-1</sup> on both surfaces between 25 and 100 K. The astrophysical implication of these results is that on timescales shorter than that estimated for the formation of a complete monolayer of water ice on a grain, aggregation of water ice will result in a non-uniform coating of water, hence leaving bare grain surface exposed. Other molecules can thus be formed or adsorbed on this bare surface.

## Introduction

Reactive accretion on grain surfaces is the dominant formation route for water (H<sub>2</sub>O) in the interstellar medium (ISM). In addition, other molecular species agglomerate onto interstellar dust grains in molecular cloud environments as the cloud transitions from diffuse through translucent to dense and the temperature falls. Such dust grains have been shown to be composed of silicates and/or carbonaceous species.<sup>1,2</sup> In the early stages of mantle formation on a dust grain, H<sub>2</sub>O coverage will be small but will grow with time. As the temperature continues to decrease, reaching temperatures as low as 8 K in some objects,<sup>3</sup> a mantle composed of many different molecules can be observed.<sup>4</sup> H<sub>2</sub>O is the major component of these icy mantles and as such has been the focus of much research.<sup>2</sup> More recently, H<sub>2</sub>O ice has been directly detected on comet 67P/Churyumov-Gerasimenko by the Rosetta mission<sup>5</sup> confirming the icy grain origins of these primitive bodies.

Temperature programmed desorption (TPD) experiments on H<sub>2</sub>O have consistently shown zero order desorption kinetics on amorphous silica (aSiO<sub>2</sub>),<sup>6</sup> sapphire,<sup>7</sup> graphene<sup>8</sup> and both polycrystalline and single crystal metals (e.g. Au<sup>9</sup> and

Ru(0001)/Al(001)<sup>10</sup>). Other work has indicated that fractional orders of desorption occur from graphite surfaces<sup>11</sup>. TPD experiments probe the balance of surface-adsorbate and adsorbate-adsorbate interactions and the results of such experiments allow us to determine whether the H<sub>2</sub>O-H<sub>2</sub>O interaction is favoured over the H<sub>2</sub>O-surface interaction. The H<sub>2</sub>O-H<sub>2</sub>O interaction being dominant is indicative of multilayer desorption. Ballistic deposition<sup>12</sup> (hit-and-stick adsorption), as likely occurs at the cryogenic temperatures of the ISM,<sup>13</sup> should lead to a mixture of isolated monomers or random sized groups of H<sub>2</sub>O on the grain surface. Therefore H<sub>2</sub>O would need to become mobile on the surface at some temperature if bulk islands are to be formed. This means that H<sub>2</sub>O must de-wet the surface before desorption ensues. Infrared spectroscopy provides one way of observing the mobility of water on surfaces, and hence of observing wetting *versus* de-wetting behaviour. This paper will report on such investigations on both amorphous silica (aSiO<sub>2</sub>) and highly oriented pyrolytic graphite (HOPG) surfaces.

Further consideration of the mobility of water on grain surfaces should be given with regard to the Onion Model of icy grain mantles.<sup>14,15</sup> This model describes how a dust grain is initially uniformly covered by a polar layer, predominantly H<sub>2</sub>O, which in turn is covered by an apolar layer, made up of species such as carbon monoxide (CO). Complex organic molecule (COM) synthesis is then energetically-promoted within this layered structure.<sup>16</sup> This model naturally assumes limited, if not zero, mobility of H<sub>2</sub>O on grain surfaces in the cold, dense environments present in the ISM. Any significant mobility would therefore impact this model and the nature of the chemical nano-factories responsible for the chemical

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## ARTICLE

Journal Name

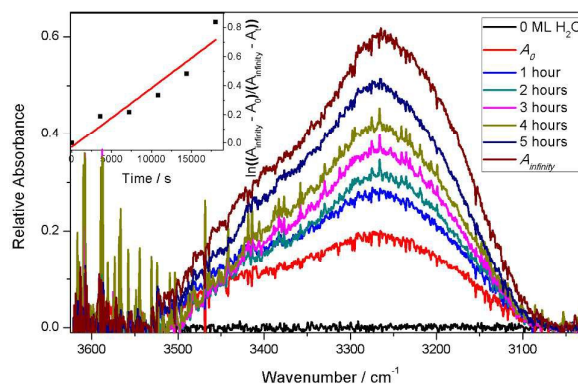
complexity of the Universe. This paper will investigate this phenomenon and report on results that challenge the current view.

## Experimental

Parallel experiments were conducted on aSiO<sub>2</sub> and HOPG surfaces at Heriot-Watt University (HWU) and the University of Sussex (UoS), respectively. The apparatus and general experimental methods employed in both laboratories have been described in detail previously.<sup>11,17,18</sup> Herein only details specific to the reported measurements are given. Before any measurements, substrates were annealed to 220 K at HWU and 250 K at UoS to ensure a surface free from H<sub>2</sub>O and other likely volatile contaminants. A quantity of H<sub>2</sub>O equivalent to 0.5 of a monolayer (ML) was dosed onto the aSiO<sub>2</sub> substrate at the system base temperature 17 K (HWU). On HOPG, a slightly larger amount of water was dosed (1.5 ML) at 24 K (UoS). This was the minimum dose possible on the less reflective HOPG surface that gave a good signal/noise ratio with reflection-absorption infrared spectroscopy (RAIRS). Since water does not wet HOPG<sup>11</sup>, then this slightly larger dose of water does not affect the behaviour on the surface compared to that expected for a lower dose (0.5 ML). Following H<sub>2</sub>O dosing on both surfaces, the background pressure was reduced to  $2 \times 10^{-10}$  mbar, or lower, as determined by quadrupole mass spectrometry (QMS). The H<sub>2</sub>O film was annealed from base temperature to the temperatures specified in the text for a total annealing time of 500 s in 100 s steps, at each stage the sample was left to cool to base temperature. After this stage a final annealing step was conducted at 100 K for 20 min. The only exceptions to this were the measurements done at the HWU base temperature where spectra were collected with an hour on average between each spectrum reflecting the slower evolution of the de-wetting process on aSiO<sub>2</sub> at these temperatures. Further experiments on H<sub>2</sub>O films annealed at 100 K for upwards of two hours, to produce a fully islanded H<sub>2</sub>O environment, were also carried out. RAIR spectra were collected with a 1 cm<sup>-1</sup> resolution as the sum of 512 scans at the base temperature of the system. The typical timescale for recording spectra was approximately 12 minutes. This time has been incorporated appropriately into the experimental timescales near base temperature. At elevated temperatures, the spectroscopic change during the RAIR measurements was considered small compared to that induced by the annealing and is ignored.

## Results and Discussion

Fig. 1 shows the time evolution of the RAIR spectra of 0.5 ML H<sub>2</sub>O on aSiO<sub>2</sub> at 18 K in the region of the O-H stretching vibrations, vOH (3000–3600 cm<sup>-1</sup>). It is clear that the band intensity increases, from the initial value of  $A_0$ , with increasing time over the period of the isothermal spectroscopic experiment. An additional small increase following the final anneal to 100 K (labelled as  $A_{\text{infinity}}$  in Fig. 1) is also observed. In experiments on HOPG at 24 K and above, a similar increase in the band intensity was also observed. Given the length



**Figure 1:** Time-resolved RAIR spectra of the vOH stretch region of 0.5 ML H<sub>2</sub>O on aSiO<sub>2</sub> at 18 K. The time between each RAIR spectrum was one hour as this was determined to be the average time between scans when H<sub>2</sub>O is annealed at the other temperatures investigated. The sharp peaks are due to gas-phase H<sub>2</sub>O in the optics boxes on the air side of the UHV apparatus. Inset is the kinetic analysis using eqn 1. Figure also found in reference [19].

of these experiments, in excess of 6 or more hours, additional experiments have been conducted that confirm that the growth of the vOH band intensity is not simply due to uptake of H<sub>2</sub>O (partial pressure  $\ll 10^{-12}$  mbar) from the residual gas in the chamber.

The observed increase in the vOH band intensity could be interpreted in two ways; (i) an increase in the number of oscillators on the surface or (ii) an increase in the band strength. Given a fixed initial H<sub>2</sub>O dosage, the surface concentration will not change during the experiments (background dosing experiments confirm this as shown in the supplementary information). Hence only an increase in the vOH band strength can explain the observations. It is well-known that hydrogen-bonded vOH exhibits higher band intensity than non-hydrogen-bonded vOH.<sup>20</sup> Hence, the experimentally observed vOH band intensity increase can only be interpreted as arising from an increase in the degree of hydrogen bonding in the deposited H<sub>2</sub>O film.

How might this increase in the degree of hydrogen bonding occur? Ballistic deposition of H<sub>2</sub>O at 17 K gives rise to a population of isolated H<sub>2</sub>O molecules, small polymeric H<sub>2</sub>O clusters and larger, three-dimensional water islands on the aSiO<sub>2</sub> surface. The spectroscopy of small H<sub>2</sub>O clusters is well-known and features are found in the vOH region on the high frequency (above 3500 cm<sup>-1</sup>) side of the band.<sup>21,22</sup> However, the presence of gas phase water features from the purge gas in the external IR optics inhibits such observations in Fig. 1.

In the ballistically-deposited amorphous solid water (ASW) islands, typical oxygen atom connectivity is between 2 and 3 water molecules, *cf.* 4 in crystalline ice and compact ASW.<sup>23,24</sup> The hydrogen bond network is thus fragmented and hence the bulk vOH band intensity is reduced. Thermal treatment of such porous ASW films results in hydrogen bond connection, prompting a variety of effects such as volatile gas trapping<sup>25,26</sup> and changes in the electrical properties of the ice film<sup>27</sup> in addition to increasing bulk vOH band intensity. This occurs in a highly non-linear fashion with temperature from around 25 K to approximately 80 K, producing a

compact ASW film with a relatively constant  $\nu\text{OH}$  band intensity and profile until crystallisation commences at around 130 K.<sup>28</sup>

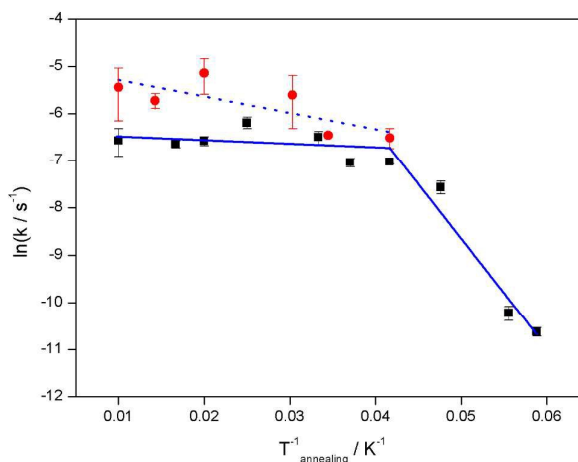
Clearly any observed increase in  $\nu\text{OH}$  band intensity at temperatures below 25 K is associated with agglomeration of isolated  $\text{H}_2\text{O}$  and small  $\text{H}_2\text{O}$  clusters into the larger ASW islands. Above this temperature both agglomeration and hydrogen bond network formation can occur in parallel.

The inset in Fig. 1 is a first order kinetic analysis of the IR data using a well-established method;<sup>29</sup>

$$\ln\left(\frac{A_{\text{infinity}} - A_0}{A_{\text{infinity}} - A_t}\right) = kt \quad (1)$$

where the  $A$  are band intensities integrated from 3050 – 3600  $\text{cm}^{-1}$ . The rate constant obtained from Fig. 1 and those obtained from measurements at elevated temperatures on  $\text{aSiO}_2$  and HOPG substrates are given in Table 1.

Arrhenius analysis of the data in Table 1 yields Fig. 2. The data are clearly non-Arrhenius overall. However, we can interpret this data as two regions of Arrhenius-like behaviour. The rising (low temperature) edge yields an activation energy of  $1.8 \pm 0.3 \text{ kJ mol}^{-1}$  on  $\text{aSiO}_2$ . A well-known assumption concerning diffusion of molecules on surfaces is that the activation energy for diffusion is 10 - 15% of the binding energy.<sup>30</sup> This assumption holds true for atoms and molecules such as C, N and CO on metal surfaces.<sup>30</sup> The activation energy for thermal desorption of  $\text{H}_2\text{O}$  is  $43.9 \pm 2.0 \text{ kJ mol}^{-1}$  on an  $\text{aSiO}_2$  surface<sup>6</sup> and  $39.9 \pm 0.8 \text{ kJ mol}^{-1}$  on HOPG<sup>11</sup> and involves breaking two hydrogen bonds of about  $21 \text{ kJ mol}^{-1}$  per hydrogen bond, corresponding well to known hydrogen bond strengths of about  $20 \text{ kJ mol}^{-1}$ .<sup>31</sup> The  $1.8 \pm 0.3 \text{ kJ mol}^{-1}$  determined in this work for diffusion below 25 K on  $\text{aSiO}_2$  is consistent with that of diffusion of  $\text{H}_2\text{O}$  on an  $-\text{OH}$  terminated surface (estimated to be around  $2 \text{ kJ mol}^{-1}$  on water from TPD data as explained). The  $\text{aSiO}_2$  substrate is known to be  $-\text{OH}$  terminated<sup>32</sup> and hence the data in



**Figure 2:** Arrhenius analysis of the kinetics of  $\text{H}_2\text{O}$  agglomeration on  $\text{aSiO}_2$  (filled squares) and HOPG (filled circles) with lines representing the best linear fit for the two surfaces along with error bars. The solid lines represent the fits to the two  $\text{H}_2\text{O}$  on  $\text{aSiO}_2$  regions as discussed in the text.

the rising edge of Fig. 2 are consistent with diffusive agglomeration of  $\text{H}_2\text{O}$ .

Above 25 K, the data in Fig. 2 shows a plateau forming on both the HOPG and  $\text{aSiO}_2$  surfaces, corresponding to an activation energy of  $0.0 \pm 0.1 \text{ kJ mol}^{-1}$ . Clearly the behaviour of the  $\text{H}_2\text{O}$  ice is not dependent on the identity of the surface, at least for the surfaces investigated. The plateau in the data could be interpreted as having a small negative gradient, but the uncertainties in the data on both surfaces suggests that  $0.0 \text{ kJ mol}^{-1}$  is realistic. Over this temperature range the structural reorganisation in ASW cannot be monitored with IR spectroscopy due to the experimental conditions limiting observations of the H-dangling bond. ASW undergoes a phase change from porous (p) ASW to compact (c) ASW starting at a temperature of about 38 K<sup>33</sup> and a further phase change from c-ASW to crystalline solid water (CSW) at above 130 K.<sup>24,34</sup> The p-ASW to c-ASW phase change has been observed to occur at temperatures from 25 K to around 80 K,<sup>33,35-37</sup> but might occur over a wider temperature range. Indeed, recent data suggest that the p-ASW to c-ASW phase change proceeds over the temperature range from 40 K to 100 K.<sup>38</sup> These data therefore suggest that the activation energy for the p-ASW to c-ASW phase transition is  $0.0 \text{ kJ mol}^{-1}$ .

Experiments looking at the de-wetting of 0.5 ML ( $\text{aSiO}_2$ ) or 1.5 ML (HOPG) of  $\text{H}_2\text{O}$  at higher temperatures approaching the compact to crystalline phase change and desorption temperature were also attempted. However sharpening of the  $\nu\text{OH}$  band with the onset of crystallisation and loss of  $\text{H}_2\text{O}$  from the surface invalidated our simple analysis.

How can we reconcile the two mechanisms proposed for the spectroscopic changes reported herein? If both diffusive agglomeration and hydrogen bond network formation are observed as the data suggest, then at low temperatures ( $<25 \text{ K}$ ) the rate of the latter is sufficiently slow to be small in comparison to the rate of diffusive agglomeration and we hence only measure the temperature dependence of the diffusive process. In contrast, in

$T_{\text{anneal}} / \text{K}$ ( $\pm 0.3 \text{ K}$ )	$k(\text{aSiO}_2) / \text{s}^{-1}$	$k(\text{HOPG}) / \text{s}^{-1}$
17	$2.432 \times 10^{-5} (\pm 8\%)$	-
18	$3.640 \times 10^{-5} (\pm 15\%)$	-
21	$5.188 \times 10^{-4} (\pm 14\%)$	-
24	$8.894 \times 10^{-4} (\pm 4\%)$	$1.488 \times 10^{-3} (\pm 21\%)$
27	$8.788 \times 10^{-4} (\pm 9\%)$	-
29	-	$1.572 \times 10^{-3} (\pm 1\%)$
30	$1.508 \times 10^{-3} (\pm 15\%)$	-
33	-	$3.703 \times 10^{-3} (\pm 51\%)$
40	$2.046 \times 10^{-3} (\pm 12\%)$	-
50	$1.392 \times 10^{-3} (\pm 10\%)$	$5.865 \times 10^{-3} (\pm 36\%)$
60	$1.300 \times 10^{-3} (\pm 11\%)$	-
70	-	$3.289 \times 10^{-3} (\pm 16\%)$
100	$1.400 \times 10^{-3} (\pm 27\%)$	$4.330 \times 10^{-3} (\pm 51\%)$

**Table 1:** Rate constants derived from analysis of time-resolved RAIRS data on 0.5 ML of  $\text{H}_2\text{O}$  deposited on  $\text{aSiO}_2$  and 1.5 ML of  $\text{H}_2\text{O}$  on HOPG at 17 K (HWU) and 24 K (UoS) at the listed annealing temperatures



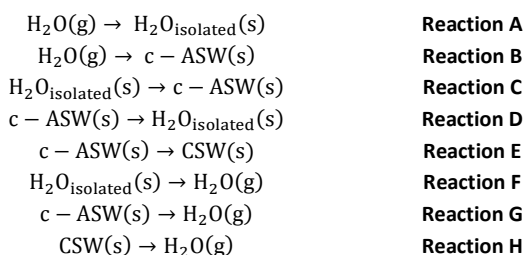
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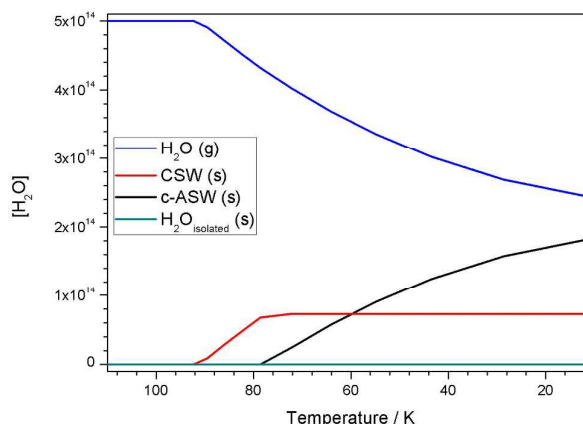
the plateau region, the rate of diffusive agglomeration is high; fast enough that the process is effectively complete within the timescale of the first annealing and spectrum measurement cycle and the dosed H<sub>2</sub>O is in the form of three-dimensional islands. Therefore in the high temperature (>25 K) region, this measurement probes only the hydrogen bond network formation process in the clustered H<sub>2</sub>O environments.

### Astrophysical Implications

From an astrochemical standpoint, the work reported herein is relevant to cooling environments in the ISM, *i.e.* a diffuse cloud collapsing into a dense cloud where bare dust grains will accrete icy mantles as the environment cools. The cloud collapse timescale has been estimated to be at least 10<sup>6</sup> years<sup>39,40</sup> and as this happens the temperature will gradually fall from about 100 K to 10 K as the density increases.<sup>2</sup> As this occurs, molecules will adsorb onto dust grains and the resulting freeze-out process is thought also to occur on a 10<sup>6</sup> year time scale.<sup>41</sup> The cooling process is non-linear and the rate can vary from 1 K per 10<sup>2</sup> to 10<sup>4</sup> years. As the environment cools, H<sub>2</sub>O initially accretes into the high temperature crystalline (CSW) phase; only growing as c-ASW and finally p-ASW as the temperature falls significantly further. The principal source of H<sub>2</sub>O is recombination of O and H atoms on grain surfaces.<sup>42-45</sup> However, non-thermal desorption of H<sub>2</sub>O from grain surfaces followed by re-adsorption<sup>46</sup> and gas phase formation routes<sup>47</sup> represent key additional H<sub>2</sub>O sources. Enthalpy release from accretion reactions on H<sub>2</sub>O ice surfaces and energetic processing<sup>19</sup> ensure that compaction of ASW occurs at a rate competitive with ASW deposition. Hence, an agglomeration model can be constructed, recognising that H<sub>2</sub>O prefers to be in c-ASW or CSW islands. The resulting kinetic model can be presented as below:



The adsorption processes in the scheme above, **Reactions A and B**, are assumed to have unit sticking coefficients. In these steps, H<sub>2</sub>O is assumed to adsorb at random and with equal probability as isolated molecules and small clusters; and in larger three dimensional islands. **Reaction C** represents the agglomeration process investigated in this work and utilises the activation energy reported in this work. **Reaction D** represents the reverse of the agglomeration process which necessarily must proceed *via* hydrogen bond scission, *cf.* the desorption processes in **Reactions F to H**, with activation energies ranging from 45 – 47 kJ mol<sup>-1</sup> and an associated pre-exponential factor of 10<sup>28</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>.<sup>6</sup> **Reaction E** is crystallisation. This mechanism is assumed to be



**Figure 3:** Simulation of H<sub>2</sub>O adsorption onto an interstellar dust grain during cloud collapse and freeze-out as the temperature falls from 110 K to 10 K. Gas phase molecules (g) will either adsorb as isolated or clustered H<sub>2</sub>O. As the temperature is above the energy needed for de-wetting, isolated molecules instantly become crystalline or clustered depending on temperature. The simulation has been done for 0.5 ML H<sub>2</sub>O with an  $E_{\text{act}}$  for diffusive agglomeration (de-wetting) of 1.8 kJ mol<sup>-1</sup> and a pre-exponential factor of 10<sup>12</sup> s<sup>-1</sup> with a cooling rate of 1 K per 10<sup>2</sup> years. Figure also found in reference [19].

independent of the surface upon which the H<sub>2</sub>O ice is growing, consistent with our data at temperatures above 25 K.

Fig. 3 shows the time evolution of the reaction mechanism above. We assume, for simplicity, that H<sub>2</sub>O accretes directly from the gas phase rather than incorporating a full surface formation mechanism from H and O atoms. As the temperature falls and H<sub>2</sub>O is adsorbed as either isolated or clustered H<sub>2</sub>O, no isolated molecules are found on the surface as seen in the H<sub>2</sub>O<sub>isolated</sub>(s) trace. Agglomeration occurs on an extraordinarily short timescale compared to deposition, meaning that H<sub>2</sub>O islands form from the earliest cooling times to later stages when cold cores have been formed. At early times, H<sub>2</sub>O grows as crystalline islands, but as the temperature continues to fall, amorphous island growth begins.

The cooling rate used in the simulation in Fig. 3 was 1 K per 10<sup>2</sup> years; at the faster end of cloud cooling in the ISM. However, reducing the cooling rate to 1 K per 10<sup>4</sup> years will only shift the temperature scale to slightly higher temperatures and reduce accretion into amorphous islands. Changing the cooling rate, however, has no impact on the agglomeration of isolated H<sub>2</sub>O and small H<sub>2</sub>O clusters into larger island environments.

What is the astrophysical impact of the agglomeration, or de-wetting, process highlighted in this work? First of all, H<sub>2</sub>O will not accrete as a uniform thin film on a grain surface, but will instead form three-dimensional islands leaving exposed grain surface. In the case of silicate grains, this will be the bare silicate surface likely terminated by –OH groups. However, silicate dust grains in the ISM are subject to space weathering and iron nanoparticle production<sup>48</sup> and so the silicate grain surface might be peppered with metallic atoms and clusters. As the grain cools further, the question arises as to which surface the second most abundant condensed phase species, carbon monoxide (CO), would adsorb on to, and TPD experiments provide the answer. Firstly, CO will form a monolayer

on both SiO<sub>2</sub> and H<sub>2</sub>O surfaces before building a multilayer. At low CO exposures, equivalent to a coverage of 0.1 ML or less, the binding energy of CO on the aSiO<sub>2</sub> surface is greater by 1 – 2 kJ mol<sup>-1</sup> than on the c-ASW surface.<sup>6,24,49</sup> Pontoppidan *et al.*<sup>50</sup> have observed CO in various H<sub>2</sub>O poor environments in the ISM. Three features were found at 2143.7 cm<sup>-1</sup>, 2139.9 cm<sup>-1</sup> and 2136.5 cm<sup>-1</sup>. The first two features can be assigned to multi-layers of CO. The latter feature was left unidentified. It has been suggested that this unassigned feature could be CO in a CH<sub>3</sub>OH matrix,<sup>51</sup> but an assignment of CO directly adsorbed to the silicate surface<sup>6</sup> is also compatible with the results of the investigation and model suggested herein.

On carbonaceous surfaces, the situation is less clear. On graphite, evidence suggests that low coverages of H<sub>2</sub>O do not wet the surface and instead form islands, leading to fractional orders in desorption kinetics.<sup>11</sup> Subsequent film growth, however, exhibits zero order kinetics which would be consistent with H<sub>2</sub>O forming multilayers as on aSiO<sub>2</sub>. Hence, on graphitic grains, the exposed surface will also consist of bare patches of carbon. On graphene surfaces (and it is very likely on very large polycyclic aromatic hydrocarbon (PAH) molecules), zero order desorption kinetics are observed at all exposures,<sup>8</sup> cf. aSiO<sub>2</sub>. Hence, the bare carbonaceous surface might also be exposed in these circumstances as H<sub>2</sub>O island growth proceeds. Adsorption of CO then leads to cluster growth on graphite<sup>52</sup> and graphene surfaces while forming a monolayer on water surfaces.<sup>53</sup>

CO is a precursor to the formation of many complex organic molecules (COMs).<sup>2</sup> Hydrogenation produces formaldehyde (H<sub>2</sub>CO) and methanol (CH<sub>3</sub>OH). In the presence of ammonia (NH<sub>3</sub>), produced like H<sub>2</sub>O by reactive accretion and likely exhibiting similar wetting and de-wetting interactions due to its hydrogen bonding nature, energetic processing will give rise to a multitude of species including pre-biotic species as complex as ribose.<sup>54</sup> However, our results suggest initial CO accretion, and hence COM formation, is likely not to occur on bulk H<sub>2</sub>O surfaces. The preference for CO binding to silicate surfaces at early times in COM formation is, in fact, likely to be reinforced given recent observations of efficient non-thermal desorption which indicate that H<sub>2</sub>O ice surfaces are unlikely to accrete significant CO due to an exciton-promoted desorption mechanism that is absent on silicate surfaces.<sup>55</sup> Rather than the classic Onion Model therefore, a more accurate model would be of domains that are H<sub>2</sub>O-rich and domains that are CO-rich with both domains interacting directly with the dust grain surface. The nature of COMs produced would then be dependent on the domain. This might present an additional opportunity to use COMs as a clock to star formation as the CO-rich domains are likely to desorb at lower temperatures, and hence at earlier times, in star-forming clump collapse.

## Conclusions

The presented work has focused on the initial stages of icy mantle growth on dust in the ISM. As explained in the introduction, TPD experiments have shown that H<sub>2</sub>O clusters at all exposures on

various surfaces.<sup>6-11</sup> This indicates that the H<sub>2</sub>O-H<sub>2</sub>O interaction is favoured over the H<sub>2</sub>O-substrate interaction. This clearly suggests that H<sub>2</sub>O mobility on the model surfaces is thermally activated. Using RAIRS, we have measured the activation energy for H<sub>2</sub>O agglomeration of isolated molecules and small clusters to larger three-dimensional islands to be 1.8 ± 0.3 kJ mol<sup>-1</sup> below 25 K. Above 25 K, agglomeration is rapid and complete in the initial experimental timescale and our observed activation energy of 0.0 ± 0.1 kJ mol<sup>-1</sup> is associated with hydrogen bond formation processes in fragmented hydrogen bonding networks such as produced by ballistic deposition.

A key consequence of these observations is that the established Onion Model of COM growth, *i.e.* a layered polar and apolar structure subject to energetic and thermal processing, should be revised. The alternative model forced on us by our observations of H<sub>2</sub>O agglomeration, coupled with evidence gleaned from laboratory observations on efficient non-thermal processes, is that COM formation likely occurs in three-dimensional domains physically separated on the grain surface.

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